

variety of crops. Pot tests indicated that addition of about 200 p.p.m. of copper from copper sulfate produced a toxic reaction in soils low in copper, but otherwise comparable to Alsatian vineyard soils, which were found to contain as much as 400 p.p.m. of copper. Among the crops tested, vines were most resistant to copper toxicity; clover and alfalfa were most sensitive.

Symptoms of copper poisoning were found in southern France in spinach and gladiolus grown in a field once occupied by a peach orchard that had been sprayed heavily for many years with Bordeaux mixture. Only the parts of the field having quite acid soil (pH 4.5 to 4.7) were affected; the copper content of that soil was 98 to 130 p.p.m.

Future research in disease control and soil fertility with copper-containing compounds should evaluate the residual effects, because nearly all the copper applied to crops will normally be fixed in the few inches near the surface of the soil.

## Manganese and Soil Fertility

G. Donald Sherman

Plants require tiny amounts of manganese to grow and mature properly. Otherwise they fail as completely as if they lacked the major elements.

Paul M. Harmer, in research work at Michigan Agricultural Experiment Station, reported a 100-bushel increase an acre in yields of potatoes after the manganese-deficient soil in which they were growing received a liberal application of manganese sulfate. He obtained an increase of 561 bushels of potatoes an acre after he had applied

a small amount of manganese sulfate in Bordeaux sprays.

Cereal crops grown on manganese-deficient soils often fail to yield enough to replant the field. The cereals need less manganese than alfalfa does. Peppermint, spearmint, and rhubarb grow normally on a soil in Michigan that had too little manganese for onions, potatoes, alfalfa, oats, and beans.

Manganese-deficient soils have been found in many parts of America.

Chemical analyses have disclosed that the manganese content of plants of the same crop vary greatly.

Manganese with the aid of iron assists in the synthesis of chlorophyll, since all chlorophyll tissues have the highest concentrations of manganese.

In research with field peas in Michigan, I found that manganese controls the state of oxidation of several oxidation-reduction systems in the plant. Conditions existed in manganese-deficient plants that favored the oxidation of iron, ascorbic acid, and glutathione to their respective oxidized forms. In a normal plant these constituents occur in their reduced form.

The staining of iron in plant tissue showed the deposition of ferric iron, an insoluble form of iron, in the veins of pea leaves of a manganese-deficient plant, whereas the normal plant gave no test for ferric iron in the veins of the leaves. The normal leaf had an even distribution of ferrous iron, an available and active form of iron, throughout the leaf tissue; the manganese-deficient leaf showed only small amounts of ferrous iron in tissue near the veins. Recalling the pattern of the chlorosis (yellowing) developed on pea leaves, the results showed an almost complete absence of iron in the chlorotic, yellow parts of the leaf. The manganese-deficient leaves contained more iron, which supports the function of manganese in the movement of iron in plants.

SYMPTOMS of a deficiency of manganese have been established for most of the agronomic and horticultural crops by growing the plants in purified cul-

tures devoid of manganese and in soils known to be deficient in manganese.

Plants that have net-veined leaves generally develop a deficiency symptom of a definite and similar pattern. Manganese deficiency leads to a chlorosis in the interveinal tissue of their leaves. The veins remain dark green; the color persists even when the chlorotic parts die. Some plants of this group develop symptoms similar to deficiency symptoms of iron and zinc and to the toxicity symptom produced by too much boron.

Plants with leaves that have parallel veins developed a general chlorotic condition and secondary symptoms—such as a gray speck of cereals and Pahala blight of sugarcane.

Symptoms of manganese deficiency commonly are known by descriptive popular names—in cereals, gray speck, white streak, dry spot, and leaf spot; in field peas, marsh spot; in sugarcane, streak disease and Pahala blight; and in spinach and beans, yellow disease.

Gray speck in oats is typical of the symptoms in other cereals and grasses. The manganese-deficient plants develop a grayish lesion on the base of the leaf. The lesion increases in size and becomes bright yellow or orange at the edge of the leaf—the halo stage. Tissue within the lesion dies and is known as dry speck or dry spot condition. The leaf tip is green. The basal part is dead. Chlorosis of all the green tissue follows rapidly.

Investigations in Michigan by Dr. Harmer and me showed that different types of manganese-deficiency symptoms develop in different varieties of oats. We grew four varieties of oats—Gopher, Wolverine, Iogold, and Huron—on the same manganese-deficient soil under identical conditions. Huron was the least susceptible to the manganese deficiency. Gray speck on it was confined to small, oval, grayish spots on the leaves. Long, grayish lesions, which changed to the halo appearance, and necrosis of the leaf developed in Wolverine, a very susceptible type.

Too much available manganese in

the soil also harms plant growth. Excessive amounts exist in some soils of Kentucky and Connecticut. Tobacco and other crops grown on them develop a severe chlorosis. Pineapples on some soils in Hawaii become chlorotic because of too much manganese. One can detect a spotted condition (caused in the early stages by the uneven distribution of chlorophyll) by holding the leaf toward the sun.

AMONG THE FACTORS that influence the availability of manganese in the soil is the basic chemistry of manganese in the soil. Seldom is a soil depleted of its manganese by leaching to the point that it cannot adequately supply the plant with available manganese. The factors that contribute to the development of a manganese-deficient condition are of two general groups: Deficiencies produced by the chemical conditions in the soil and those produced by biological factors.

Soils with a reaction above pH 6.0 favor the oxidation of manganous manganese, a divalent form of manganese. The oxidation-reduction conditions in strongly acid soils favor the reduction of manganic manganese (the insoluble, high-valence form) to the manganous manganese, an available form.

The manganese can be leached from a strongly acid soil, but leachates from an alkaline soil show only traces of manganese. The manganese content of strongly acid soils subject to much leaching is low, especially if the leaching occurs during cool weather. An example is the soils along the Atlantic coast in the Southeastern States. Despite their low content of manganese, these soils in their native condition did not produce manganese-deficient conditions in respect to plant growth. A soil capable of reducing manganic manganese can maintain a low but adequate supply of manganous manganese, which is easily replaceable, since the equilibrium favors the available manganous manganese.

The liming of strongly acid soils to an alkaline reaction has been the com-

monest cause of manganese deficiency. An acid soil with a low content of active manganese should receive only enough lime to change the reaction to pH 5.7 to 6.0. The application of lime to a slightly acid organic soil that does not need lime will depress the growth of some crops, among them onions, potatoes, beets, cereal crops, legumes, and tree crops.

The continuous application of lime to soils having a high content of easily reducible manganic oxide may produce a manganese-deficient condition. The reapplication of lime will cause a steady depletion of the easily reducible manganic oxide as a result of its conversion to inert manganic oxides.

Acid organic soils can be made alkaline by methods other than the direct application of lime.

The burning of organic soils, especially those well supplied with lime, produces an alkaline condition. The reaction of organic soils after burning often ranges from pH 6.8 to 8.2. Before burning they were able to supply the plant with enough available manganese for normal growth. After burning, they have a high capacity for the oxidation of manganese and its subsequent fixation as inert oxides. Thus a manganese-deficient condition is brought about. Organic soils that have been deeply burned require heavy applications of manganese fertilizers.

The alkalinity of some organic soils in Michigan has been caused by alkaline water from springs. An alkalinity so produced causes a soil to become manganese-deficient by the reversion of its oxidation system in respect to manganese.

Imperfectly drained mineral soil of a high organic content may naturally overlime itself in some places. A manganese deficiency is produced in the spots that fluctuate between well-drained and waterlogged conditions between seasons. The soil has a high amount of calcium and magnesium. The waterlogged condition during a part of the year and the subsequent withdrawal of the water remove the

manganous manganese. After the withdrawal of the excess water, conditions for rapid oxidation of manganese rapidly set in and cause a deficiency.

The leaching of strongly acid soils removes the manganous manganese from the soil because the conditions in them favor the reduction of the manganic manganesc. Perhaps they lose so much manganese from overleaching that too little manganese is left to support normal plant growth.

Regardless of how small the active manganese content of strongly acid soils may be, this manganese exists under conditions favorable to its maximum availability. It is doubtful if many cases of manganese deficiency are due directly to this cause, but it is the indirect factor that sets the stage for many of the manganese deficiencies in soils. It is often the agent that reduces the copious supply in the parent material from which the soils were formed.

Several investigators have proved that bacteria are responsible for the inability of plants to obtain available manganese from the soil.

F. C. Gerretsen, of the Netherlands, reported that a gray speck disease would not develop on a manganese-deficient soil when formalin was added to the soil. He concluded that gray speck was caused by certain bacteria in the soil. G. W. Loeper and R. J. Swaby, Australian soil scientists, have shown that bacteria can oxidize manganous manganese to manganese dioxide.

MANGANESE EXISTS in the soils in several forms, which determine its availability to plants.

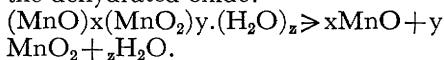
The exchangeable and water-soluble manganese (which is the divalent manganous ion) is the only form available to the plant. The manganous-manganic equilibrium and the capacity of the soil to oxidize manganese control the level of available manganese. When a manganous salt is added to an alkaline media, a white precipitate is formed; it soon turns brown and settles out rapidly. It has been identified as manganous hydroxide, which under-

goes partial oxidation to the hydrated manganic oxide, an insoluble form of manganese. The addition of a reducing agent will reverse this reaction to the hydroxide form, the white precipitate.

Substantial evidence supports the existence of this system in the soil: First, because the rate of fixation is related to the concentration of hydroxyl ion rather than bacterial activities and, secondly, the existence of the hydrated oxide can be established by its properties. The addition of reducing agents will cause the increase in concentration of manganous ions. The dehydration of the hydrated oxide will cause a splitting of manganous oxide and manganese dioxide.

A manganese cycle in soils has been developed and its basic principles are: Manganous manganese  $\rightleftharpoons$  colloidal hydrated  $\text{MnO} \cdot \text{MnO}_2 \rightleftharpoons$  inert  $\text{MnO}_2$ .

The reaction can be reversed by the addition of a reducing agent. Dehydration will cause the following split of the dehydrated oxide:



The reaction is considered to be reversible. Thus the treatment of manganese deficiency can be approached by using these fundamental reactions.

First, the deficient condition can be corrected by direct applications of manganous salts. If the soil has a high capacity for the fixation of manganese, their efficiency will be low.

Secondly, the fixation capacity of the soil can be reduced by applying acid-forming material, which reduces the hydroxyl concentration. The formation of the hydroxide is the first step in the fixation, and subsequent oxidation of the manganese to the hardly soluble hydrated oxide can be reduced by decreasing the hydroxyl concentration of the soil through its acidification.

Lastly, manganese deficiency can be corrected by the application of reducing agents. The application of hydroquinone, stannous chloride, hydrazine sulfate, and sodium azide have corrected manganese-deficient soil by increasing the available manganese.

Likewise the correction of manganese toxicity can be accomplished by taking advantage of the manganese cycle in soils. The soluble and available manganese can be reduced by increasing the hydroxyl concentration in soil by the application of lime and by using mulches to prevent dehydration through exposure to wind and sun.

SEVERAL METHODS for the correction of manganese-deficient soils have been discovered and are recommended for use by farmers, gardeners, and greenhouse operators. The methods recommended include the direct application of manganese and indirect methods, which are based on the reversion of the manganous-manganic equilibrium.

The common method of correcting manganese deficiency is to apply manganese salts to the soil. The rate of application is determined by the type of soil and by its fixation capacity.

Applying 50 to 100 pounds per acre of manganese sulfate to mineral soils, in which the manganese deficiency has been caused by overliming, generally will give adequate results. On soils having a slightly acid to neutral reaction, 50 to 100 pounds of manganese sulfate may be applied; 100 to 200 pounds may be put on those having a neutral to slightly alkaline reaction, and 200 to 400 pounds on soils having a strongly alkaline reaction.

At 1957 prices, manganese sulfate was the most economical means of applying soluble manganese. The use of insoluble manganese compounds, such as pyrolusite, was not considered economical because heavy applications of those compounds, finely ground, are needed to produce the same effect as smaller amounts of manganese sulfate.

An early method of correcting unproductive manganese-deficient soil was to change its reaction with the application of sulfur and other acid-forming materials. The method was economical and gave good results on organic soils. Sulfur should be used only on soils where it will bring about a relatively permanent change in reaction. Some

organic and sandy soils can be economically treated in this way; among them are peat soils; soils in Michigan, Indiana, and New York; and the soils of the Coastal Plains.

To apply manganese directly to a soil with a high-fixation capacity is an inefficient way to correct a manganese-deficient condition. Two other methods are more efficient and economical. The first is to apply manganese sulfate and sulfur together. The sulfur increases the availability of the manganese by retarding its oxidation through the reduction of the hydroxyl ion concentration. Plants growing on a manganese-deficient soil that got 400 pounds of manganese sulfate and 500 pounds of sulfur had 2.5 times more manganese in their tissues than plants growing in similar soil that got 400 pounds of manganese sulfate alone.

The other method is to apply manganese sulfate as a spray to the foliage. This method was used at the Rhode Island Agricultural Experiment Station in 1925. Many citrus growers have used it. It is economical wherever it is possible to spray the plant. The sprays have been successful on general crops, such as potatoes and cereal crops.

Manganese deficiency in a soil may be corrected temporarily by steam or sterilization by dry heat. This treatment causes a great increase in soluble manganese in the soil. The explanation for this phenomenon lies in the dehydration of the hydrated oxides, especially  $\text{MnO} \cdot \text{MnO}_2$ . The aftereffects of steam sterilization can be explained by its effect on the solubility of manganese. When a soil containing large amounts of oxides of manganese is sterilized by this means, a manganese toxicity condition is produced in respect to plant growth. This effect will disappear eventually.

The improvement of soils that have a content of soluble manganese toxic to plant growth requires a treatment that will cause the oxidation of the soluble manganese. This is done by using lime and mulch to protect hydrated oxides from dehydration.

## Trace Elements

P. R. Stout and C. M. Johnson

We hear a lot these days about trace elements. Advertisements imply they are a magic guarantee of success for any gardener and farmer. What are they?

Originally the term "trace elements" came from a custom of the analytical chemist to report the presence of elements that he could detect but were present in such small amounts as to be insignificant. Preparation of an ultimately pure chemical has never been attained because—if for no other reason—it must always come in contact with apparatus used in processing it.

The more refined grades, such as Chemically Pure, are analyzed, and the percentage of the principal chemical and the amounts of "impurities" associated with it usually are reported on the label. Elements that cannot be estimated accurately but can be detected qualitatively are simply reported as being present in trace amounts—hence the term "trace elements."

The plant physiologists ordinarily use salts available on the market to prepare the culture solutions for growing plants. In that way they determine the kind and amount of chemical elements the plants need. (A salt is a chemical compound formed when the hydrogen of an acid has been replaced by a metal. Salts are named according to the acid and the metal from which the salt is derived. Copper sulfate, for example, is a salt derived from copper and sulfuric acid.)

It often happened in earlier experiments that plants would grow ade-